OVERVIEW: ENVIRONMENTAL FATE & TRANSPORT

U.S. EPA OFFICE OF PESTICIDE PROGRAMS
ENVIRONMENTAL FATE AND EFFECTS DIVISION

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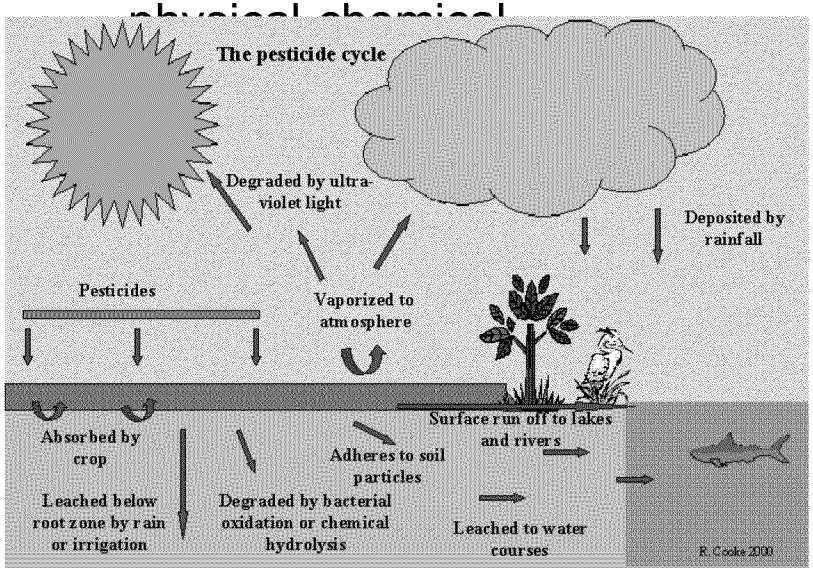
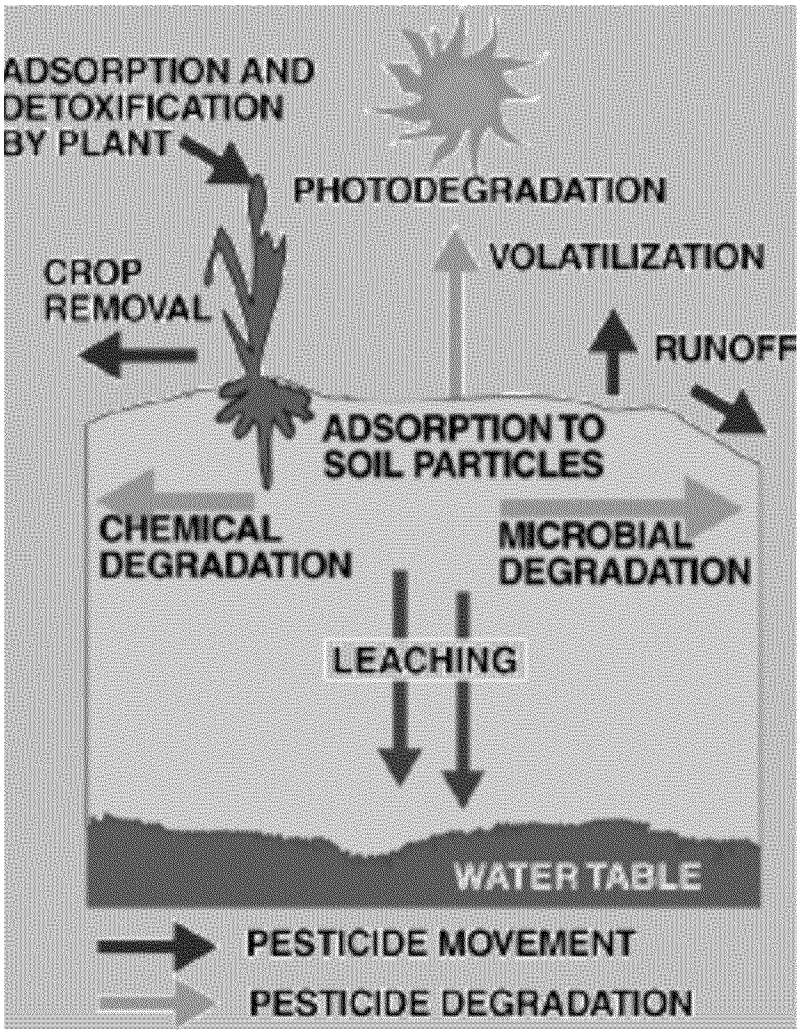
Pesticide Dissipation Conceptual Model

- Driving Factors
  - Application/Agronomic Practices
    - rate, method, timing
  - Environmental Conditions
    - weather, soil
  - Pesticide Properties
    - physical chemical





Pesticide Properties

- CFR 40 part 158
  - List required studies by use pattern and test material
  - Product Chemistry
    - identity and composition
    - physical and chemical properties
  - Environmental Fate
    - degradation studies
    - metabolism studies
    - mobility studies
    - dissipation studies
    - monitoring studies
- Purpose
  - Qualitative fate assessment
  - Identify transformation products (residues of concern)
  - Model inputs

Product Chemistry

- Identity and composition
- Physical and chemical properties
  - Partition coefficient
  - Water solubility
  - Vapor pressure

Environmental Fate

- Degradation studies
  - Hydrolysis
  - Photolysis
    - aqueous, soil, air
- Metabolism studies
  - Soil – aerobic and anaerobic
  - Aquatic – aerobic and anaerobic
- Mobility studies
  - Leaching
  - Volatility – laboratory and field
- Dissipation studies
  - Terrestrial and Aquatic
- Monitoring studies
  - Groundwater and Surface Water*

Study	Guideline Number
Hydrolysis	835.2120
Aquatic Photolysis	835.2240
Soil Photolysis	835.2410
Air Photolysis	835.2370
Aerobic Soil (ASM)	835.4100
Anaerobic Soil	835.4200
Aerobic Aquatic	835.4300
Anaerobic Aquatic	835.4400
Leaching and Adsorption/ desorption	835.1230 835.1240
Laboratory Volatility	835.1410
Field Volatility	835.8100
Terrestrial Field Dissipation (TFD)	835.6100
Aquatic Field Dissipation	835.6200

Degradation Studies: Hydrolysis

- Estimate the rate of Abiotic degradation of compounds in water as a function of pH; identify and measure degradates
- Study design
  - 30 day study in the dark
  - compound is added to water, minimal co-solvents
  - carried out at 3 pH values, 5, 7, & 9 and 3 temperatures 10, 25, 50
  - typically at least 5 measurements
- Endpoints
  - hydrolysis half-lives
  - identify degradates and maximum concentrations
- Utility in risk assessment
  - inputs into aquatic models
  - used to estimate degradation in water bodies and aquifers

Degradation Studies: Photolysis in Water

- Estimate the rate of abiotic degradation of compounds in water as impacted by light; identify and measure degradates
- Study design
  - 30 day study
  - compound is added to water with minimal co-solvents
  - at least 5 concentration measurements over time
  - uses natural sunlight or simulates natural light
  - must include a dark control
- Endpoints
  - photolysis half-lives (difference in rate constants between the light and dark control)
  - identify degradates and maximum concentrations
- Utility in risk assessment
  - inputs into PWC
  - used to estimate degradation in surface water (clear, shallow water bodies)
  - elucidate potential drinking water treatment effects

Photolysis in Soil

- Estimate the rate of abiotic degradation of compounds in soil as impacted by light; identify and measure degradates
- Study design
  - 30 day study
  - compound is applied to moist soil
  - at least 5 concentration measurements over time
  - uses natural sunlight or simulates natural light
  - must include a dark control
- Endpoints
  - photolysis half-lives (difference in rate constants between the light and dark control)
  - identify degradates and maximum concentrations
- Utility in risk assessment
  - not routinely used in modeling
  - affects surface soils (upper 2 mm), in open canopy conditions. Most applicable to a scenario where a pesticide is applied pre-plant

Metabolism Studies: Soil

- Estimates the rate of biotic degradation of chemical in soil as impacted by microbes in soil under aerobic (with O_2) and anaerobic (without O_2) conditions
- Study design
  - 120 day study; (longer if half-life is not reached within 120 days)
  - Compound is applied to moist soil; must include 4 different soil series
  - At least 5 measurements over time
  - Degradate analysis is required for at least one soil
  - Conducted under dark conditions
  - Aerobic – conducted with presence of atmospheric O_2
  - Anaerobic – begins at aerobic conditions, must achieve and maintain anaerobic conditions (O_2 strictly excluded)
- Endpoints
  - half-lives reported for all 4 soils
  - identify degradates and maximum concentrations
- Utility in risk assessment
  - aerobic soil is a major input into aquatic exposure models
    - One of the two most important fate inputs
  - anaerobic soil metabolism study is relevant only for flooded crops *i.e.*; rice, cranberries, watercress, etc.

Metabolism Studies: Aquatic

- Estimate the rate of biotic degradation of chemical in sediment and water column under aerobic (with O_2) and anaerobic (without O_2)
- Study design
  - 120 day study; (longer if half life is not reached within 120 days)
  - conducted under dark conditions
  - aerobic – conducted with presence of atmospheric O_2
  - anaerobic – begins at aerobic conditions, must achieve and maintain anaerobic conditions (O_2 strictly excluded)
  - compound is applied to a mixed water sediment system soil; must include 2 different sediments
  - at least 5 measurements overtime (two test systems – pond, river)
- Endpoints
  - half-lives reported for all 2 test systems; degradate analysis is required in at least one soil
  - identify degradates and maximum concentrations
- Utility in Risk Assessment
  - major input into aquatic water models (total system half-lives)
    - aerobic represents degradation in the water column
    - anaerobic represents degradation in sediment
    - Further characterize partitioning

Mobility Studies: Adsorption/Desorption (Batch Equilibrium)

- Determine how much of the active ingredient (or transformation product) sorbs to soil and how much stays in the water
- Study Design
  - Adsorption
    - Combine soil (sediment), pesticide, & water
    - At least 5 soils/sediments representative of agricultural use areas (one with low organic matter) are analyzed at a minimum of 5 concentrations.
    - Filter and measure concentration of pesticide in solution and on sediment
  - Desorption:
    - Add water to above system and repeat to determine how much active ingredient desorbs from soil
  - Endpoints
    - K_f = freundlich coefficient
    - 1/n = curvature parameter
    - K_{oc} = partition coefficient as a function of organic carbon content (not all chemicals have a K_{oc})
  - Utility in Risk Assessment
    - Critical parameter in water modeling, tells us whether a chemical is likely to bind to soils or will be mobile (transport to/through waterways)
    - $C_s = K_f * C_{aq}^{1/n}$ or $C_s = K_d * C_{aq}$;

      where C_s = concentration in soil, K_f = freundlich coefficient, C_{aq} = concentration in water, 1/n = curvature parameter, K_d = distribution coefficient

Food and Agriculture Organization of the United Nations (FAO) Classification System

K_{oc} (mL/g_{oc})	Mobility Classification
<10	Highly Mobile
10-100	Mobile
100-1000	Moderately Mobile
1000-10,000	Slightly Mobile
10,000-100,000	Hardly Mobile
>100,000	Immobile

Dissipation Studies

- Type
  - Terrestrial Field Dissipation
  - Aquatic Field Dissipation
  - Forestry Field Dissipation
  - Prospective Groundwater Monitoring
- Application of active ingredient to small plot fields representative of labeled use
- Study Design
  - 1 year study; active ingredient applied to a cropped and bare ground plot; applications should be according to label directions (i.e., maximum labeled rate)
  - Measure concentrations of major and toxic degradates identified in lab studies down the soil profile over time
  - May contain different modules (depending on conceptual model)
- Endpoints
  - Concentrations at depth (as deep as 3 feet)
  - Dissipation rate as a function of time
- Utility in Risk Assessment
  - Confirms conceptual model of fate and transport based on lab data
  - Measures leaching (mobility), measures volatility (if module is considered)
  - Can identify carryover/accumulation issues

Additional or Alternative Studies or Modules

- Field Volatility Study (flux study) – measures dissipation through air via dissipation (especially useful for chemicals like the fumigants); does not include spray drift
- Long Term Field Dissipation Study – longer duration than typical TFD study
- Non GLN runoff & pond studies – measures concentration in runoff and ponds from runoff
- Spray (field) drift and laboratory droplet size

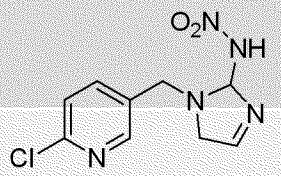
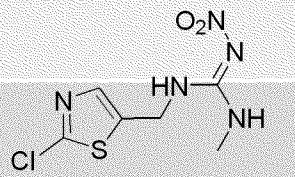
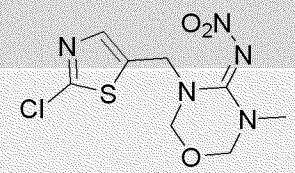
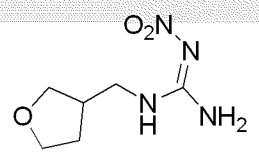
Locating Environmental Fate Data

- Example Assessment
  - https://www.regulations.gov/document?D=EPA-HQ-OPP-2015-0653-0437
- Contacts
  - https://www.epa.gov/pesticide-contacts

Chemical Classes

- Carbamates
- **Neonicotinoids**
- **Organochlorines**
- **Organophosphates**
- **Pyrethrins & Pyrethroids**
- Sulfonylureas
- Strobilurin
- **Triazines**
- Dinitroanilines
- **Phenoxy**
- Others…**Glyphosate**

Neonicotinoids

Active Ingredient	Chemical Structure	Solubility (mg/L)	Koc (mL/g)	Field Dissipation Half-life (days)	Aquatic Toxicity
Imidacloprid		514	moderately mobile	26-229	very highly
Clothianidin		327	mobile to moderately mobile	257-1,386	very highly
Thiamethoxam		4,100	mobile to moderately mobile	5-100	practically non-toxic
Dinotefuran		39,830	highly mobile to mobile	19-65	practically non-toxic

Neonicotinoids

- Use profile
  - Insecticides
    - Residential, Urban
    - Agriculture
- General toxicity profile
  - Low mammalian toxicity
  - High invertebrate toxicity including aquatic invertebrates
- Hot topic(s)
  - Bees
  - Re-registration

Neonicotinoids: Re-evaluation Timeline

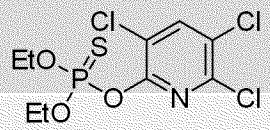
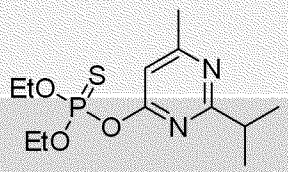
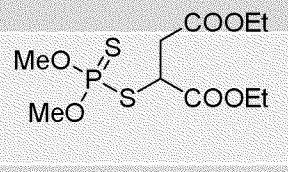
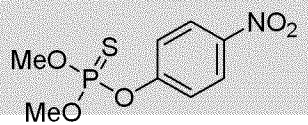
2016
- Imidacloprid preliminary pollinator assessment

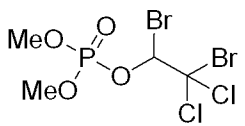
2017
- Imidacloprid assessment for taxa other than pollinators posted, and will be released for comment
- Clothianidin, thiamethoxam, and dinotefuran preliminary pollinator assessments posted, and will be released for comment
- Imidacloprid, Clothianidin, thiamethoxam, and dinotefuran human health risk assessment
- Clothianidin, thiamethoxam, and dinotefuran draft risk assessment for taxa other than pollinators

2018
- All neonicotinoids: revised pollinator/ecological risk assessments
- All neonicotinoids: proposed interim registration review decisions

2018/2019
- All neonicotinoids: interim registration review decisions

Organophosphates

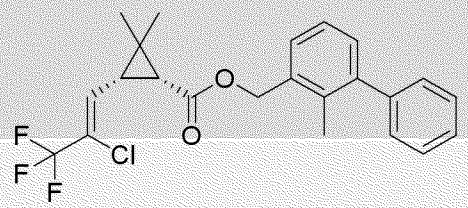
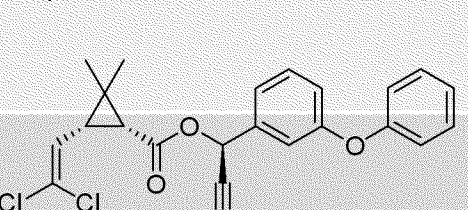
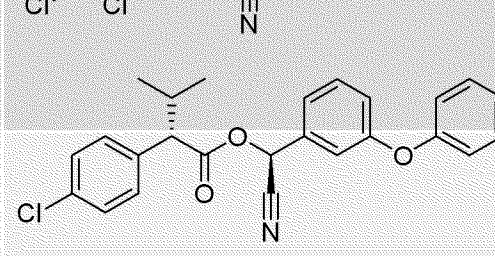
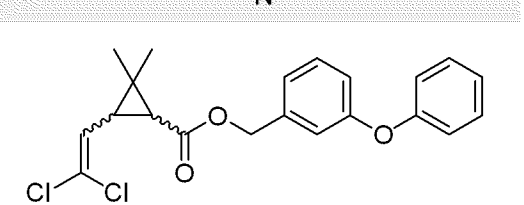
Active Ingredient	Chemical Structure	Solubility (mg/L)	Koc (mL/g)	Field Dissipation Half-life (days)	Aquatic Toxicity
chlorpyrifos		1.18	Slightly Mobile	43	very highly
diazinon		60	Slightly Mobile	40	very highly
malathion		130	Slightly Mobile	9	very highly
methyl parathion		55	Slightly Mobile	10	very highly
naled		2,000	Moderately Mobile	1	very highly



Organophosphates

- Use Profile
  - Insecticides
    - Residential, Urban
    - Agricultural
- General toxicity profile
  - High toxicity to all taxa (exception: plants***)
- Hot topic(s)
  - Neurodevelopmental effects
  - Endangered species assessment
  - Re-registration

Pyrethrins/Pyrethroids

Active Ingredient	Chemical Structure	Solubility (mg/L)	Koc (mL/g)	Field Dissipation Half-life (days)	Aquatic Toxicity
Bifenthrin		0.0001	immobile	26	very highly
Cypermethrin		0.004	hardly mobile	77	very highly
Esfenvalerate		0.0002	slightly mobile	42	very highly
Permethrin		0.006	immobile	42	very highly

Pyrethrins/Pyrethroids

- Use profile:
  - Insecticides
    - Residential Uses – dogs, spot treatment
    - Agricultural Uses – seed treatment, foliar broadcast, soil drench
- General toxicity profile
  - High toxicity to all taxa (exception: plants***)
- Hot topic(s)
  - Re-registration
  - Urban water contamination

Pyrethroid: Re-evaluation Timeline

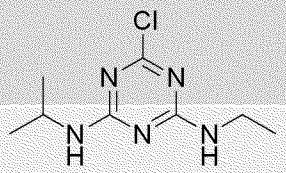
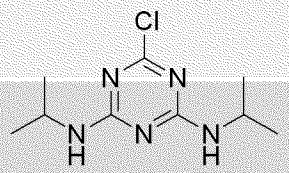
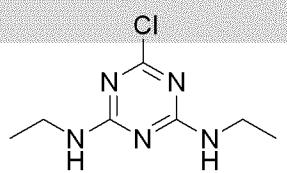
2016

- bifenthrin, permethrin, deltamethrin, cyfluthrin, cypermethrin, fenpropathrin, esfenvalerate, and lambda-cyhalothrin assessment where published
  - Highlights
    - Down the drain
    - Outdoor Urban (turf, residential, nursery, structural pest control)
    - Agricultural uses
    - Mosquito Adulticide Use Assessment (deltamethrin, permethrin, pyrethrins)
    - Tier I honey bee assessment
    - Focused on aquatic organisms (fish, invertebrates)

2017

- Public comment period on previously published assessment – on going

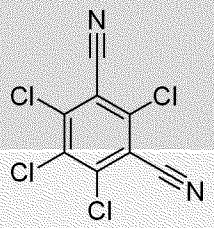
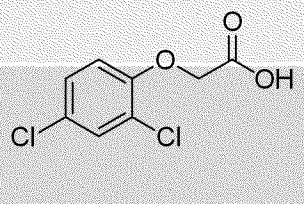
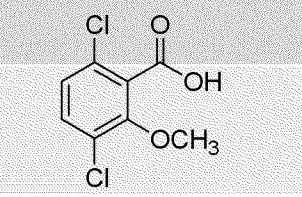
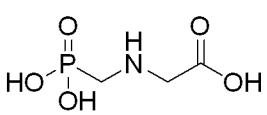
Triazines

Active Ingredient	Chemical Structure	Solubility (mg/L)	Koc (mL/g)	Field Dissipation Half-life (days)	Aquatic Toxicity
Atrazine		33	Moderately Mobile	173	high
Propazine					
Simazine		6	Moderately Mobile	60	high

Triazines

- Use profile:
  - Herbicides (one insecticide)
    - Agricultural Uses – seed treatment, foliar broadcast, soil drench
- Hot topic(s)
  - Ecological risk
    - Aquatic plant community effects
    - Amphibian effects

Others

Active Ingredient	Chemical Structure	Solubility (mg/L)	Koc (mL/g)	Field Dissipation Half-life (days)	Aquatic Toxicity
Chlorthalonil		0.8	slightly mobile	33-81	very high
2,4 D		6100	mobile		slightly toxic
Dicamba		8.6	moderately mobile	52	Moderately toxic
Glyphosate		12000	157 (K_d) immobile	1.4-142	

Conclusions

- After application pesticides are transported and transformed (environmental dissipation)
- Chemical/physical properties of pesticides chemicals can and are used to predict environmental fate
- Environmental fate data inform:
  - Human health and environmental risk assessments
  - Monitoring program design
  - Enforcement
    - pesticide use/misuse investigations

QUESTIONS

Ecotoxicity Categories for Aquatic Organisms

Toxicity Category	Aquatic Organisms: Acute Concentration (mg/L)
very highly toxic	<0.1
highly toxic	0.1 - 1
moderately toxic	>1 - 10
slightly toxic	>10 - 100
practically nontoxic	>100

Neonicotinoids

- Imidacloprid
  - A preliminary pollinator-only analysis released January 2016.
  - An aquatic risk assessment has been posted, and will be released for comment.
- Clothianidin and thiamethoxam
  - A preliminary pollinator risk assessment has been posted, and will be released for comment.
- Dinotefuran
  - A Tier 1 pollinator risk assessment has been posted, and will be released for comment.

Neonicotinoids: Preliminary Pollinator Risk Assessments

- Potential on-field risk from some use patterns appear to be low
  - Based on attractiveness and agronomic practices
  - Seed treatment uses
- Potential on-field risk from some use patterns remain uncertain: more data (expected in 2017), and further analysis will reduce these uncertainties.
  - Soil uses
- Potential on-field risk from some use patterns

- EPA intends to engage stakeholders to better inform its understanding of risks and benefits from uses that result in potential risks of concern